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THE EVOLUTION OF LIMESTONE AND DOLOMITE.
II (*Concluded*)

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PART II. CALCIUM AND MAGNESIUM IN THE PRODUCTS OF METAMORPHISM

The products of metamorphism of the rocks may be classed as solids and solutes, or residuals and losses. Residuals, the materials which remain *in situ* after a rock has suffered chemical change; losses, the materials which are dissolved, transported in solution, and redeposited elsewhere. A study of the fate of calcium and magnesium in rocks subjected to metamorphism shows that there is nearly always a marked tendency for a greater percentage loss of calcium than of magnesium. Magnesium tends to remain with the residuals to a greater degree than calcium. It will be shown that in the movement and redisposition of the residuals and losses of rock alteration, and in the reworking of these products by the same processes, again and again throughout geologic time, lies the history of a progressive enrichment of the lands in calcium and their progressive depletion in magnesium. The evidence for the selective splitting off of calcium from the parent rocks in response to metamorphic processes and the accumulation of magnesium in the residuals follows.

Materials lost by the weathering of acid igneous rocks.—The weathering[1] of acid igneous rocks results in the loss of lime, magnesia, soda, potassa, and silica. The percentage loss of the various constituents approximately follows the descending order in which they are named. For purposes of comparison alumina may be regarded as constant. The ratio of calcium to magnesium lost in the weathering of an acid igneous rock can only be given in terms of tendencies. In Table V the figures for the ratio of calcium to magnesium lost are based on the assumption that alumina has remained constant. The percentage loss of calcium averages higher than that of magnesium, a tendency generally characteristic of metamorphic processes.

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[1] Edward Steidtmann, "A Graphic Comparison of the Alteration of Rocks by Weathering with Their Alteration by Hot Solutions," *Economic Geology*, III, 381–409.

TABLE V

WEATHERING OF ACID IGNEOUS ROCKS

Rock	Ca/Mg Fresh Rock	Ca/Mg Materials Lost	Percentage Loss		Source
			Ca	Mg	
1 Granite.......	2.8	3.33	3.1	31	Watson, *Granites of Georgia*, 318
2 Granite.......	4.9	7.6	98	64	*Ibid.*, 315
3 Granite.......	2.3	5.2	88	41	*Ibid.*, 321
4 Granite.......	6.9	5	59	82	*Ibid.*, 320
5 Granite.......	3.4	4.6	43	32	*Ibid.*, 309
6 Granite.......	5	2.3	27	59	*Ibid.*, 312
7 Granite.......	5	5.2	84	83	*Ibid.*, 312
8 Granite	3.8	3	74	96	*Ibid.*, 327
9 Granite.......	3.9	4.3	78	70	*Ibid.*, 327
10 Granite.......	2.1	2.58	77	65	*Ibid.*, 325
11 Granite.......	3.3	4.8	80	54	Average Georgia
12 Granite.......	1.3	no magnesium lost	23	0	Merrill, *Rocks and Rock Weathering* (Dist. of Columbia), 207
13 Granite.......	1.3	no magnesium lost	21	0	*Ibid.*
14 Phonolite.....	3.3	12	17	5	*Ibid.* (Bohemia), 198
15 Andesite......	3.4	9.5	77	28	*Ibid.* (Grenada), 208
16 Syenite.......	1.9	1.7	67	78	Clarke, *U.S.G.S. Bull. 330*, 412
17 Gneiss........	4.2	....	100	76	*Ibid.*
Average.......	3.45	+4.12	59.7	50	

Materials lost by the weathering of basic igneous rocks.—In the weathering of basic igneous rocks, the percentage losses of calcium and magnesium average about even, in Table VI. The ratio of calcium to magnesium lost varies between wide margins, from one to infinity. The materials selected for analyses may have unequaled value in the problem.

Materials lost by the weathering of an average igneous rock.—The ratio of calcium to magnesium in an average igneous rock (Clarke) is about 1.37. The ratio of calcium to magnesium lost by its weathering, calculated on the basis of average calcium and magnesium decrements, is about 1.85.

TABLE VI
WEATHERING OF BASIC IGNEOUS ROCKS

ROCK	Ca/Mg FRESH ROCK	Ca/Mg MATERIALS LOST	PERCENTAGE LOSS		SOURCE
			Ca	Mg	
1 Diabase	2.2	4.1	25	9.5	Merrill, *Rocks and Rock Weathering* (Medford, Mass.), 218
2 Diabase	1.3	1.57	83	61	*Ibid.* (Spanish Guiana), 222
3 Basalt	1.0	.51	47	96	*Ibid.* (Crouzet, France), 223
4 Basalt	1.2	1.4	84	74	*Ibid.* (Kammer Bull.), 222
5 Diabase	.6	.6	98.7	98.2	Merrill, *Am. Geol.*, XXII, 93
6 Diabase	.64	.6	98.6	98.8	*Ibid.*, 95
7 Diorite	1.84	1.85	97.3	97.17	Merrill, *Rocks and Rock Weathering*, 225
8 Augite diorite	1.07	3.13	59	76	Morozewicz, *Zeit. Kryst. Min.*, CXXXIX, 612
9 Diabase	1.08	2.13	84	42	P. Holland and Dickinson, *Proc. Liverpool Geol. Soc.*, VII, 108
10 Boulder	.10	infinity	17.5	∞	*Helen Mine, Michipicoten* (unpub. monograph)
11 Gabbro	2.92	1.25	8.9	6	*Gabbro, Allen Junction, Minn.* (unpub. monograph)
12 Diabase	1.25	1.35	92	82	*Dike, Penokee-Gogebic* (unpub. monograph)
Average	1.27	1.62	66.3	61.5	

TABLE VII
WEATHERING OF LIMESTONE

Rock	Ca/Mg Fresh Rock	Ca/Mg Altered Rock	Source
Carboniferous limestone	148	14.9	*Ann. Geol. Rept. Arkansas* (1890), 179
Average of three analyses	1.4	.23	*Bull. 7, Va. Geol. Surv.*, 97
Knox	1.6	.01	Russell, *Bull. 52, U.S.G.S.*, 25
Galena	1.5	1.2	*Bull. 14, Wis. Geol. Surv.*, 15–16
Galena	1.5	.66	*Ibid.*
Galena	1.5	.64	*Ibid.*
Trias, France	17.2	2.38	Hilterman, *Die Verwitterungs-Produkte von Gesteinen der Trias Formation*, Frankens. *Inaugural Dissertation*, Erlangen, 1889
Plattenkalk	66.0	1.82	F. W. Pfaff, "Ueber Dolomit und seine Erstellung," *Neues Jahrb.*, XXIII, 538
Krebscheeren Kalk	61.0	1.67	*Ibid.*, 539
Average	26.5	2.61	

Materials lost by the weathering of limestones.—In the present stage of earth evolution, the principal contribution of calcium and magnesium from the weathering of the sediments probably comes from limestones. A compilation of the calcium magnesium ratio of several fresh and weathered limestones seems to indicate that the percentage loss of calcium is somewhat higher than that of magnesium and that the amount of calcium given off by the weathering of limestone greatly exceeds magnesium (Table VII).

Résumé of weathering.—It follows from the facts stated that the weathering of igneous rocks and sediments results in the loss of more calcium than magnesium and that in general the percentage loss of calcium is greater than that of magnesium.

Materials lost by dynamic metamorphism.—The dynamic metamorphism of sediments as well as igneous rocks seems to bring about certain definite chemical changes. It is difficult, however, to measure these changes since it is uncertain whether any of the elements are stable in any given case. All that can be done in the problem of determining the relative stability of lime and magnesium under dynamic condition is to compare the magnesium and calcium ratios in the unaltered materials with the calcium magnesium ratios in their metamorphosed equivalents, as shown by Table IX. Secondly, to compare the importance of calcium and magnesium in the minerals of the unaltered and metamorphosed rocks. Table IX appears to indicate that the ratios of calcium to magnesium are lower in the metamorphosed phases than in the unaltered; that is, the percentage of lime lost by dynamic metamorphism appears to be higher than that of magnesium. Concordant with this apparent chemical change is the fact that the minerals which are developed under conditions of dynamic metamorphism are predominantly magnesium and potassium bearing, rather than calcium bearing, such as the micas, chlorites, and amphiboles of Table VIII. It appears that magnesium is better adapted to dynamic condition than calcium. A selective removal of calcium from the zone of anamorphism to the zone of katamorphism and ultimately to the ocean seems to be a logical sequence.

TABLE VIII

THE PERCENTAGES OF CALCIUM AND MAGNESIUM IN CALCIUM- AND MAGNESIUM-BEARING MINERALS, CHARACTERISTIC OF DYNAMIC METAMORPHISM

Mineral	Ca	Mg	
Actinolite	9.5	13.5	Variable
Anthophyllite	0.20	28.69	Variable
Augite	11.4	8.6	Variable
Biotite	.....	14.3	Variable
Chlorite	.....	20.0	Variable
Cordierite	.....	6.1	
Hornblende	8.7	8.64	
Serpentine	.....	25.8	
Spinel	.....	11.5	
Scapolite	9.2	.....	
Tourmaline	1.14	8.9	Variable
Tremolite	9.7	14.9	Variable
Vesuvianite	25.4	1.57	Variable
Wollastonite	34.6	.....	
Zoisite	17.6	.....	

TABLE IX

DYNAMIC METAMORPHISM

Rock	Ca/Mg Original Rock	Ca/Mg Altered Rock	
Average of 12 clays and soils	1.5	....	Clarke, *Bull. 168, U.S.G.S.*, 1900, p. 296
Average of 78 shales	....	1.1	Clarke, *Bull. 330, U.S.G.S.*, 1908, p. 27
Average of 9 slates of Vermont	....	.25	Van Hise, *Mon. 47, U.S.G.S.*, 1904, p. 895
Dolomite	1.5	.03	*Mon. 46, U.S.G.S.* Altered to talc schist, pp. 215–222
Average	1.5	.66	
Gabbro	.95	.44	*Bull. 62, U.S.G.S.*, p. 76
Gabbro	.95	.10	*Bull. 62, U.S.G.S.*, p. 76. Altered more than preceding case
Greenstone	1.19	1.05	*Bull. 62, U.S.G.S.*, p. 91
Gabbro diorite	1.45	.89	*Bull. 62, U.S.G.S.*, p. 89
Average	1.13	.62	

Materials lost by contact metamorphism.—Contact metamorphism of the sediments tends to develop minerals of complex constitution and high specific gravity. The materials in excess of the requirements for the development of adapted minerals tend to be removed, and in part may reach the sea. The relative instability of calcium at contacts as compared with magnesium is suggested by the tendency toward increase in the magnesium content of altered sediments, as compared with their unaltered equivalents. See Tables X, XI, XII. The averages of the tables are misleading since they do not represent the tendency of the majority of cases.

TABLE X

CONTACT METAMORPHISM OF SLATES BY ACID INTRUSIVES

Rock	Ca/Mg Fresh Rock	Ca/Mg Altered Rock	
Chloritic phyllite....	0.13	0.22	Altered by granite (*Neues Jahrb.*, 1897, p. 156)
Slate...............	0.18	0.05	Altered by hornblende granite 50′ from contact (Hawes, *Am. Jour. Sc.*, Mt. Willard, N.H.)
Slate...............	0.18	0.14	Ditto, 15′ from the contact
Slate...............	0.18	2.3	Ditto, 1′ from the contact
Slate...............	0.18	2.1	Ditto, at contact
Yaqui Gulch........	0.39	0.87	Contact with quartz diorite (*Bull. 150, U.S.G.S.*)
Morenci shales......	0.82	0.55	Contact with porphyry (*Bull. 229, U.S.G.S.*, p. 348)
Composite..........	0.62	0.38	Of 6 slates by acid intrusives
Average..........	0.33	0.37	

TABLE XI

CONTACT METAMORPHISM OF SLATES BY BASIC INTRUSIVES

Rock	Ca/Mg Fresh Rock	Ca/Mg Altered Rock	
Composite..........	.88	.36	8 adinoles altered by diabase (Roth, *Geol.*, III)
Lenneschiefer........	.49	.56	Composite of 3 slates altered by diabase (*ibid.*)
Lenneschiefer........	.55	.30	*Ibid.*, 147
Slates..............	.09	.47	Composite of 3 slates altered by dolerite (*Crystal Falls, Mon. 36, U.S.G.S.*)
Slates..............	.19	.32	Clausthal altered by diabase dikes (Groddeck, *Jahrb. der königlich-preuss. Landesanstalt*, 1855, pp. 1–53)
Virginia............	.04	.34	By gabbro intrusive (*Mon. 43, U.S.G.S.*, 170)
Carboniferous.......	5.1	10.	Shale by peridotite dike (*Bull. 348, U.S.G.S.*, 343)
Average..........	1.04	1.75	

TABLE XII

LIMESTONE CONTACT METAMORPHISM

Rock	Ca/Mg Fresh Rock	Ca/Mg Altered Rock	
Homestake	12.7	1.01	By andesite (Leith and Harder, "Utah: The Iron Ores of the Iron Springs," *Dist. Bull. 338, U.S.G.S.*)
White Knob	18.4	74.0	By acid intrusive (Kemp, "Idaho," *Eco. Geol.*, II, 1907)
Morenci	3.98	1.03	Altered by porphyry (*Eco. Geol.*, II, 6, 1907)
Bingham	54	34	Altered by porphyry (*Prof. Paper 28, U.S.G.S.*)
Bingham	13.2	.39	Altered by porphyry (*ibid.*)
Chanarchillo	2.5	.57	Chile, altered by greenstone (Woesta, *Ueber das Vorkommen der Chlor. Jod. Brom. Verbindungen in der Natur*, Marburg, 1870)
Slightly altered limestone	7.4	2.3	F. D. Adams, *Jour. Geol.*, XVII (1909)
Slightly altered limestone	7.4	1.5	*Ibid.*

Materials lost from rocks by hot solutions.—The alteration of rocks by hot solutions along fissures also shows a marked tendency toward rapid removal of lime, and a much slower rate for the removal of magnesium. In some cases calcite, epidote, and other lime-bearing minerals develop in basic igneous rocks, but often calcium is practically absent from the secondary minerals. The compilation on page 399 has been made showing the calcium and magnesium ratio of fresh and altered rocks adjacent to ore-bearing fissures.

Résumé of calcium and magnesium in the products of metamorphism.—The data on metamorphism which have been presented indicate that the percentage loss of calcium which rocks sustain through metamorphic processes tends to be higher than that of magnesium. In fact, it could be shown that the percentage of calcium lost tends to be higher than that of any other element. Exceptions are noted, of course. In view of this tendency, Salisbury's[1] estimate that the disintegration of 55,000,000 cubic miles of average igneous rock would yield the common salt of the sea, while the disruption of three or more times as much rock would be required to yield the limestones, is suggestive.

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[1] R. D. Salisbury, "The Mineral Matter of the Sea," *Jour. Geol.*, XIII, 476–77.

TABLE XIII

THE CALCIUM MAGNESIUM RATIO OF FRESH ROCKS AND THEIR EQUIVALENTS ALTERED BY HOT SOLUTIONS ADJACENT TO ORE-BEARING FISSURES

Rock	Ca/Mg Fresh Rock	Ca/Mg Altered Rock	
Granite	1.06	.18	West Australia, Pilbara, Goldfield. Quoted by Lindgren, *Eco. Geol.*, I, 540
Amphibole schist	1.50	1.5	Kalgoorlie, West Australia. Quoted by Lindgren, *ibid.*, 530–44
Granite	1.50	67.	Lindgren and Ransome, "Cripple Creek," *Col. P.P. 54, U.S.G.S.*, 194
Phonolite	5.40	2.4	Ditto
Granodiorite	1.94	5.0	Lindgren, "Placer Co. Cal.," *A.I.M.E.* (1901), 586–87
Amphibole schist	.34	1.7	Ditto
Limestone	116.	17.1	Limestone altered by hot springs. Spurr, "Aspen, Colo.," *Mon. 31, U.S.G.S.*, 210
Andesite	1.64	.35	J. E. Spurr, "No. 2 Tonopah," *Nev. P.P. 42*, p. 216
	....	.67	J. E. Spurr, "No. 3 Tonopah," *ibid.*
	....	.35	J. E. Spurr, "No. 4 Tonopah," *ibid.*
	..	.54	J. E. Spurr, "No. 5 Tonopah," *ibid.*
	....	.57	J. E. Spurr, "No. 6 Tonopah," *ibid.*
	....	.28	J. E. Spurr, "No. 7 Tonopah," *ibid.*
	....	.00	J. E. Spurr, "No. 8 Tonopah," *ibid.*
Monzonite porphyry	2.1	.17	Lindgren, "Clifton-Morenci," *P.P. 43*, pp. 168–69
	....	.24	Ditto, No. 3
	....	.09	Ditto, No. 4
	....	5.1	Ditto, No. 5
Monzonite porphyry	1.4	3.2	Boutwell, "Bingham District," *P.P. 38*, p. 178
Diorite	1.4	1.03	"Willow Creek District, Idaho," *20 Ann. Rept. U.S.G.S.*, Pt. III, 211–32
Hornblende andesite	2.59	2.71	"No. 3, Hauraki Gold Fields," *Eco. Geol.*, IV (1909), 637
Hornblende dacite	2.67	−2.86	"No. 2, Hauraki Gold Fields," *ibid.*, 638
Butte granite	1.95	.62	"No. 2, Sericitized Granite," unpublished investigation, University of Wisconsin
Butte granite	1.95	.53	"No. 8, Granite Mineralized," unpublished investigation, University of Wisconsin
Butte granite	1.95	.77	"No. 9, Hard Silicified Granite," unpublished investigation, University of Wisconsin

It is obvious that if metamorphism continued until all rocks were separated into end products, the residuals remaining in place and the materials lost transported to the sea, it would result in a running down of the calcium content of the lands, and a relative increase in magnesium.

In the deep zones of high pressure and temperature, where there is only slight mobility of the residual materials, this result may be reached and perpetuated for a long time until, in the course of geologic ages, they finally become the shallow zones of low temperature and pressure. Here the residuals of metamorphic processes as well as the materials lost are forever in a state of motion in response to the movements of the atmosphere and the hydrosphere, controlled by gravity and the sun. Thus the products of metamorphism are redistributed into the sedimentary rocks, and these in turn are reworked and redistributed. In this redistribution lies the potentiality of an increase of the ratio of calcium to magnesium of the lands with geologic time.

Has sedimentation increased the ratio of calcium to magnesium of the lands during geologic time?

The sedimentary rocks are derived from other sediments and from igneous rocks, ultimately they are derived from igneous rocks. Clarke's average igneous rock is generally accepted as representing the approximate composition of the primitive lithosphere. The criticism may be offered that this average is necessarily not based on a study of the volumetric importance of the various igneous rock types in the primitive lithosphere. It has also been maintained that the igneous rocks themselves are very largely derived from the fusion of sediments, which may be so but has not been proven. The recurrence of certain predominant igneous rock types at various times and places suggests that the composition of magmas has not been materially influenced in the way which one would expect from regional subfusion of sediments. It seems probable that the primitive lithosphere had a composition between rhyolite and basalt, which is expressed in Clarke's average. Approximations, not finalities, seem all that can be hoped for in this problem.

By an ingenious graphic method, W. J. Mead[1] estimates that the average igneous rock is equivalent to shales, sandstones, and limestones of Clarke's average compositions in the ratio of 80:11:9.

F. W. Clarke[2] has made a similar estimate, based on average chemical compositions, in which he distributes the average igneous rocks into shales, sandstones, and limestones in the ratio of 80:15:5.

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[1] W. J. Mead, "Redistribution of the Elements in the Formation of Sedimentary Rocks," *Jour. Geol.*, XV (1906), 238.

[2] F. W. Clarke, "Data of Geochemistry," *Bull. 330, U.S.G.S.* (1908).

An earlier estimate by Van Hise[1] divides the sedimentary rocks into 65 per cent shales, 30 per cent sandstones, and 5 per cent limestones.

A computation made by myself, using Mead's method, shows that a composite Georgia[2] granite made from Watson's analyses is nearly equivalent to a mixture of composite Georgia clay (Watson's) and average sandstone (Clarke's) in the ratio of 55:45, not enough lime and magnesia being present to be available for limestone. Another computation by myself shows that a composite basic rock made up from composites of diabase, gabbro, basalt, and peridotite in the ratio of 6:6; 6:1 is equivalent to average shale and limestone (Clarke's) in the ratio of 88:12. The upshot of all these computations and estimates seems to be that the predominant igneous rock types are equivalent to a large percentage of clastics, predominantly mud or shale, and a relatively small percentage of limestone, hence the same would be true of the primitive lithosphere, regardless of whether it was entirely rhyolite or entirely basalt.

Under the theory of the stability of oceanic and continental segments, the redistribution of the primitive lithosphere into sediments may have taken place along one or the other of two uniformitarian directions. The redistribution materials may have been deposited upon the continents and in the oceans in such proportions as to leave the composition of the lands unchanged. This might be termed "integral" redistribution, because it leaves the composition of the lands as a whole as it was before. Obviously "integral" redistribution of the redistribution materials to the *n*th power would not change the composition of the lands. But redistribution has certainly changed the composition of the lands with respect to one element at least—sodium. That the lands contain less sodium now than in the past, in consequence of leaching and the accumulation of non-sodiferous sediments on the lands, is clearly shown by Becker[1] in his recent contribution, "The Age of the Earth."

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[1] C. R. Van Hise, "Treatise on Metamorphism," *Mon. U.S.G.S.*, XLVII (1904), 940.

[2] Watson, *Bull. No. 9-A*, *Geol. Survey of Georgia.*

Instead of leaving the composition of the lands as before, redistribution might result in a selective withdrawal of certain elements from the lands and possibly the retention of others. This may be termed "selective" redistribution. Redistribution has been selective with respect to sodium, resulting in a progressive decline in the contribution of sodium from the lands to the sea. It probably has been selective with respect to potassium, causing only a slight accumulation of potassium in the sea as compared with sodium. The question is raised here whether selective redistribution may not have caused an actual progressive increase in the calcium content of the lands and a correlative progressive decrease in magnesium, which in turn may have been connected with a similar progressive change in the ratio of calcium and magnesium contributed to the sea, and of the calcium and magnesium carbonates deposited in the sea. It has been pointed out that regardless of whether the primary lithosphere was rhyolite or basalt, redistribution would result in a large proportion of clastics, predominantly mud, and a small proportion of limestone. If redistribution has been integral with respect to clastics and limestones, it would follow that the sediments exposed on the continents are predominantly clastics and subordinately limestones. This test will be applied here to the continental interiors, the continental margins, the epicontinental seas and the deep seas, so far as the progress of my studies permits.

The geologic record of the continental interiors.—The greater portion of the surface of the lands consists of sediments. Major Tillo[2] estimates that the Archaean and younger eruptives constitute only 24.3 per cent of the known area of the continents. It follows from obvious reasons that the greater part of the calcium and magnesium now being delivered to the sea by the rivers comes from the sediments exposed on the lands, and the proportions of calcium and magnesium in the rivers will be roughly proportional to the amount of calcium and magnesium in the sediments and to the relative solubility of calcium- and magnesium-bearing minerals in the sediments.

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[1] G. F. Becker, "The Age of the Earth," *Smithsonian Inst. Miscellaneous Collections,* LVI (1910), No. 6.

[2] Quoted from Berghaus' *Atlas der Geologie* (1892).

In his discussion of "The Metamorphic Cycle," C. K. Leith[1] says:

> Averages of sections made from field observations give uniformly a lower[2] percentage of shales and higher of limestones. An average of twenty-one sections from different parts of the United States shows thirty per cent of limestone. If the difference of proportion determined by the chemical[3] and field methods is a real one, as inspection of the data seems to indicate, the significant questions are raised, (1) whether there may not be a concentration of limestones on the continental areas, their complimentary shales and muds being in the deep sea, (2) whether limestone may not be concentrated in the upper, observed part of the lithosphere, because of its known inability to remain in the deep seated zones of high pressure and temperature.

That the Paleozoic sediments of the Mississippi Valley show a surprising concentration of limestones amounting to from 23.6 to 66.6 per cent of the sections averaged and a marked deficiency of shales and sandstones is brought out in an admirable study made by Miss F. W. Carter.[4] The results of this study are compiled in Table XIV.

TABLE XIV

TABLE SHOWING THE RELATIVE PROPORTIONS OF LIMESTONES, SHALES, AND SANDSTONE IN THE PALEOZOIC OF THE MISSISSIPPI

State	Limestone	Shale	Sandstone
Pennsylvania........	23.6	47	25
Alabama...........	41.3	23	35.5
Ohio...............	33.2	41.4	23.6
Michigan...........	42.2	38.3	19.1
Indiana............	39	30.3	30.6
Wisconsin..........	52	38.3	9.5
Minnesota..........	50.9	40.4	11.5
Iowa...............	61.1	29.1	9.7
Missouri...........	66.6	22.8	10.4
Oklahoma..........	31.7	52.2	16.7
Colorado—eastern...	27.5	4.8	57.6
Colorado—central....	57	20.9	21.9

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[1] C. K. Leith, "The Metamorphic Cycle," *Jour. Geol.*, XV (1907), 304.

[2] Lower than the percentage gotten by distributing an average igneous rock into average sediments.

[3] The chemical method of W. J. Mead (*op. cit.*).

[4] Unpublished thesis (1910), University of Wisconsin.

The composition of the limestones of the Paleozoic of the Mississippi Valley averages that of magnesian limestones, with a lime percentage higher than that of a normal dolomite.

The unconformities in the Paleozoic of the Mississippi Valley represent the removal or lack of deposition of both limestones and clastics, mostly clastics, as follows from the compilation below, also made by Miss Carter (Table XV). Both sedimentation and erosion seem to have worked hand in hand toward the concentration of limestones.

TABLE XV

TABLE OF UNCONFORMITIES IN THE PALEOZOIC OF THE MISSISSIPPI VALLEY

Location	Extent	Kind of Rock Eroded	Amount Eroded	Summary
First base of St. Peter sandstone	Widespread	Limestone L. magnesian	Less than one-half thickness	Took off limestone
Second base Maquoketa shale	Widespread	Galena limestone	Negligible	
Third top of Silurian	Widespread	Salina and Niagara limestone	Slight	
Fourth top of Mississippian	Widespread	Limestones and shales	Much	
Fifth ever since Carboniferous	Widespread	Shale, sandstone, and some limestone	More than preceding combined	Took off more clastics than limestones in preceding

It seems to follow that the sediments of the Mississippi Valley were either derived from sediments already high in limestones, or else the complementary muds have been carried elsewhere, to the margins of the continents perhaps. But even granted that they were derived from sediments high in limestones, it is difficult to escape from the conclusion that ultimately redistribution was selective. Concentration of limestones on the lands began somewhere at some time. A selective withdrawal of muds from the continents began somehow, for the Paleozoic sediments of the Mississippi Valley show a proportion of limestones far in excess of the proportions gotten by redistributing either rhyolite or basalt, the two dominant magmatic differentiates.

A remarkable preponderance of limestone is also evident from the following averages made from sections in the interior of China, described by Blackwelder in *Researches in China*.

Section	Shales	Sandstone	Limestone	Unknown
	Per cent	Per cent	Per cent	Per cent
Sinian system, Shantung, Northeastern China (Cambro-ordovician, unconformity on limestone)	14	...	86	
Shantung (Carboniferous)	71	...	29	
Shantung, Permo-Mesozoic	36	40	....	24
Shansi-Wu-Tai District. Average of Paleozoic (unconformity on limestone)	Clastics 19.5	...	80.5	
Eastern Ssi Chuan and Lower Yang Tzi Gorges. Paleozoic section (unconformity on top of upper Carboniferous limestone)	17.6	6.5	75.6	

The continent of Europe shows a similar dominance of limestones over clastics. In the southern province of sedimentation, the record is nearly continuous from the Cambrian to the Pliocene, and presents a proportion of limestones far in excess of the ratio gotten by distributing an average igneous rock into the sediments.

Another peculiarity of the sediments on the continental interiors is that they are generally less disturbed and less anamorphosed than the sediments on the margins of the continents. The marginal distribution of mountain ranges and volcanoes harmonizes with this generalization. The fact that the sediments of the continental interiors are generally less anamorphosed than those of the margins is significant in regard to their chemical denudation. Anamorphism tends to cause the decomposition of carbonates and the development of complex silicates, but the silicates are less easily dissolved, hence the relatively small amount of anamorphism of these sediments increases their importance as sources of calcium and magnesium in river waters.

Taking the lime and magnesia contents of Clarke's average sediments merely as objects of illustration, the following table suggests how important the concentration of limestone on the continents may be in changing the ratio of calcium and magnesium in the river waters from what it would be if the lands had the composition either of an average igneous rock, rhyolite or basalt.

TABLE XVI

Rock	Percentage CaO	Percentage MgO	Ratio CaO:MgO	Percentage of Average Sediment (Mead)	Percentages of Paleozoic Sediments of Missouri (Carter)
Shales (Clarke)....	3.11	2.44	1.2:1	80	22.8
Sandstone (Clarke).	5.50	1.16	4.7:1	11	10.4
Limestone (Clarke)	42.57	7.89	5.3:1	9	66.6
Average igneous rock (Clarke)....	4.79	2.39	1.4:1	..	....
Rhyolite (Osann)..	1.43	.38	3.7:1	..	....
Basalt (Osann)....	8.91	6.03	1.4:1	..	....

The ratio of lime to magnesia in the average sediment is about the same as in the average igneous rock, 1.4:1. The ratio of lime to magnesia in the Paleozoic sediments of Missouri would be about 4:1 if their composition is like that of Clarke's average sediments. The numerical values are not positive, but they point to the probability that the concentration of limestones on the continental interiors may have had a surprising effect on the lime and magnesia content of river waters, and ultimately on the chemical deposits of the sea.

The record of continental margins.—Chamberlin[1] has pointed out that the sediments which fringe the margins of the continents are characterized by a greater number of unconformities and more intense metamorphism than the sediments of the continental interiors. The imperfections of the marginal record therefore make it impossible to make a fair comparison between the limestone content of the marginal sedimentary column and that of the continental interiors. It is perhaps significant that the marginal sediments of late Tertiary and more recent times are predominantly clastic, which suggests a synchronous relation between continental expansion and the deposition of clastics.

Deposition within the 100-fathom line during continental expansion.—It is significant that in the present geologic epoch of continental expansion, the area of the epicontinental sea is limited to about 10,000,000 square miles, perhaps less than a third of what it has been during periods of great marine expansion. It is also significant that the present period of continental expansion is not favorable to limestone building in epicontinental seas. The preponderance of clastics now forming on the shallows surrounding the lands is such that the sediments within the 100-fathom line are generally spoken of as consisting entirely of muds and sands, although important limestone-building areas are found around Florida, Yucatan, and on the Australian Great Barrier reef. The dominance of clastics seems to be related to climatic conditions and the rejuvenation of streams which has accompanied the rejuvenation of the lands. But shallow, epicontinental seas in times past have been important areas of limestone deposition when their expanse was greater than now.

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[1] T. C. Chamberlin, *Geology*, III, 526.

Deposition beyond the 100-fathom line.—The area of the ocean is estimated by Murray as 143,259,300 square miles. The littoral and shallow-water zones comprise about 10,062,500 square miles, consequently the deep-sea area covers about 133,186,800 square miles. The calcareous deep-sea deposits of terrigenous origin, coral muds, and coral sands have an area of about 2,556,800 square miles or about 1.9 per cent of the deep-sea area. Of the pelagic deep-sea calcareous deposits, the globigerina ooze comprises 49,520 square miles, pteropod ooze 400,000 square miles, or a total of 49,920,000 square miles, 37 per cent of the deep-sea area. The total area of deep-sea calcareous deposits thus constitutes about 39 per cent of the deep-sea area.

The terrigenous non-calcareous muds have a total area of about 16,050,000 square miles, or about 11 per cent of the deep sea. The pelagic non-calcareous deposits have an area of about 64,670,000 square miles, approximately 48 per cent of the area of the deep sea, of which red clay represents 51,500,000 square miles and diatom ooze 10,880,000 square miles. In total, the non-calcareous deep-sea deposits cover about 59 per cent of the deep-sea area.

The content of calcium and magnesium in samples of deep-sea deposits collected by the Challenger expedition has been compiled in Table XVII.

It shows that calcium is more abundant than magnesium, the ratio of calcium to magnesium being about 13:1. The report on deep-sea deposits by the Challenger expedition concludes that the average calcium carbonate content of the deep-sea bottom is about

TABLE XVII

Deposit	Mean Depth Fathoms	Ratio of Calcium to Magnesium	Magnesium Percentage	Calcium Percentage	Approximate Percentage of Area of Ocean Bottom
Coral sand	176	19.2:1	1.8	34.6	coral ss and muds 1.40
Green sand	449	30:	.64	20.0	.59
Green mud	513			10.20	
Red mud	623	43:1	.64	19.55	.07
Coral mud	740	......	....	34.2	.....
Vocanic muds	1,033	......	....	8.15	.42
Volcanic sands		16:1	.99	16.03	
Pteropod ooze	1,044	76:1	.42	32.2	.28
Blue mud	1,411	4.7:1	.56	2.71	10.00
Diatom ooze	1,477	28:1	.32	9.17	7.60
Globigerina ooze	1,996	19:1	1.38	26.3	34.50
Radiolarian ooze	2,094	2:1	1.84	4.19	1.60
Red clay	3,730	5:1	.70	3.48	36.00
					92.66

37 per cent, of which fully 90 per cent is derived from the remains of calcareous organisms living near the surface of the sea. However, the 37 per cent calcium carbonate at the sea bottom merely represents the difference between solution and deposition. Solution of the calcareous remains according to the Challenger report is a very important process, resulting principally from the generation of carbonic acid by the decay of the dead organisms.

It is to this fact that the decrease in calcium carbonate with depth is supposed to be due. See Tables XVII and XVIII.

TABLE XVIII

TABLE SHOWING RELATION OF $CaCO_3$ TO DEPTH OF WATER, TAKEN FROM CHALLENGER REPORT

	Average Percentage
14 cases under 500 fathoms	$CaCO_3$ 86.04
7 " from 500 to 1,000 "	$CaCO_3$ 66.86
24 " " 1,000 to 1,500 "	$CaCO_3$ 70.87
42 " " 1,500 to 2,000 "	$CaCO_3$ 69.55
68 " " 2,000 to 2,500 "	$CaCO_3$ 46.73
65 " " 2,500 to 3,000 "	$CaCO_3$ 17.36
8 " " 3,000 to 3,500 "	$CaCO_3$ .88
2 " " 3,500 to 4,000 "	$CaCO_3$ .00
1 " over 4,000 "	$CaCO_3$ trace

The calcium content of the ocean is a variable controlled by its solution and deposition in the ocean and its introduction from the lands. It is therefore barely possible that calcium is now accumulating in the sea, partly from direct chemical reasons, the calcium content of the ocean being below the saturation point, and partly because the shallow-water area, most conducive to the biochemical deposition of calcium carbonate, is relatively limited during the present epoch of continental expansion; and partly because the shallow waters bordering the continents are now considerably polluted by mud and other land débris which depreciates the shore zone as a habitat for lime-secreting organisms. Present climatic conditions also restrict the life zones favorable to shallow-water limestone deposition. Murray and Irvine[1] have concluded from experimental evidence that the calcium carbonate of the sea is probably nearly constant in quantity, since the precipitating agents of the sea probably maintain a balance between the introduction and deposition of calcium carbonate, despite the fact that the calcium carbonate content of the sea is below the saturation point. Whether or not calcium carbonate is actually accumulating in the sea seems uncertain, when the wide range of precipitating conditions controlled by the temperature, pressure, and the relative abundance of living and decaying organisms is considered. Nor would annual analyses of sea water give any clue, since it has been estimated that it would require about 680,000 years to accumulate the calcium carbonate now in the sea at the present rate of contribution from the land, a fact which in itself may be significant of the possibilities in this problem. Judging from the selective solubility of calcium carbonate with respect to depth, it seems that the widening of the epicontinental sea to approximately 30,000,000 square miles during the Carboniferous, as estimated by Chamberlin, must have given a tremendous impetus to the deposition of calcium carbonates on these extensive shallows. Here wave agitation might cause mechanical precipitation, and would minimize the carbonic acid content of the waters which might otherwise be influenced by organic decay. Evaporation would tend to cause concentration. Thus in shallow waters, calcium carbonate may become so unstable through these and other causes as to result in direct chemical precipitation as shown by the well-known case described by Willis[1] in the Everglades off the Coast of Florida and that of Lyell[2] in the mouth of the Rhone. In shallow, warm waters near the lands, the deposition of calcium carbonate through lime-secreting organisms is very much more rapid than in deep waters.

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[1] *Proc. Roy. Soc. Edinburgh*, XVII (1890). 81.

While 90 per cent of the accumulations of calcium carbonate on the floor of the present deep sea come from the skeleta of free-swimming organisms which thrived within the photobathic zone in shallow waters, the remains of both the free-swimming and benthos organisms augment the rate of accumulation. Furthermore, the chances for the preservation of skeleta are many times better in shallow water than in the deeps, as shown by the decrease in the calcium carbonate content of marine deposits with depth. In sinking through miles of water, the remains of pelagic organisms often dissolve before reaching the bottom. Not only is there a very clear dependence of abundant limestone deposition on shallows in the present seas, but from the physical evidence of ripple marks, etc., Schuchert concludes that North American Paleozoic limestones were probably all deposited in less than 300 feet of water. The food supply is another very important factor which attracts lime-secreting organisms to warm, clear, shallow seas near the continents.

The activity of the lime-secreting organisms would be further stimulated by the climatic moderation and uniformity which seem to accompany periods of oceanic expansion. The warming of the seas, consonant with oceanic expansion according to Chamberlin's hypothesis, would diminish its capacity for carbonic acid and decrease the solubility of calcium carbonate. But the shallow epicontinental sea, it seems, would be most susceptible to solar heating, hence from a combination of causes, mechanical, physical, chemical, and organic, limestone building in the shallow seas would probably be intensified in more than arithmetical ratio to the increase in the area of shallow water. The total contribution of calcium from the land would be lessened because of the decreased area of the lands. Could not a depletion of the calcium carbonate content of the sea result from intensified deposition on the submerged continents? What then? The solubility of the calcium carbonate toward the shallows from the deeps, a process now in operation as shown by the results of the Challenger expedition, would be accelerated. The selective accumulation of limestones on the continents as shown by geologic sections would be consummated.

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[1] *Jour. Geol*. I (1893), 512.

[2] *Principles of Geology* (12 ed.), I, 426.

Significance of the deposition of muds in the ocean basins.—The composition of river muds is variable, depending upon the composition of the lands over which the rivers flow. The longer the delta region of a river, in general, the smaller probably will be the amount of soluble materials in the muds. The Nile and Mississippi muds may be regarded as typical of the larger streams of the world. In an analysis of Mississippi mud[1] the ratio of lime to magnesia is 1.11:1 (Table XIX). The ratio of lime to magnesia in an analysis of Nile[2] mud is 1.82:1.

TABLE XIX

TABLE SHOWING LIME AND MAGNESIA RATIOS OF NILE AND MISSISSIPPI MUDS

	CaO Percentage	MgO Percentage	Ratio of CaO to MgO
Nile mud...........	4.85	2.64	1.82
Mississippi mud.....	1.83	1.64	1.11

The analyses of Nile and Mississippi muds show a relatively high content of magnesia, as compared with other sediments. It follows that if any large proportion of muds is lost from the lands through deposition in the ocean basins, it would mean a selective abstraction of magnesia from the lands, considering the quantitative importance of the muds. The ratio of suspended material to total dissolved solids in the Mississippi at Memphis, according to Dole's yearly average, is 2.3:1. Mellard Reed has estimated that the proportion of suspended to dissolved materials in the river waters of the world is 66:33, or 2:1. Approximately one-half of the dissolved material is calcium carbonate. The ratio

[1] By C. H. Stone, *Science*, XXIII (1906), 634.

[2] Analysis D., *Bull. 330, U.S.G.S.*, 429.

of suspended materials or muds to calcium carbonate is about 4.4:1, which argues for a great deficiency in muds in the sediments now forming as compared with the proportion got by distributing average igneous rock under conditions most favorable to the deposition of clastics, namely, the condition of continental expansion. This is in line with the fact that the present lands represent an accumulation of limestones. Of the muds now carried to the sea, the major portion are deposited on the continental shelves, and therefore have the potentiality of again becoming a part of the land surface. J. W. Barrell[1] estimates that from 50 to 70 per cent of the solids brought down to the sea by rivers is deposited within the 100-fathom line. But many of the large world streams, the Amazon, the Congo, Indus, Ganges, and others, have their terminations near the 100-fathom line. Amazon muds have been traced to a distance of 300 miles from the mouth. Barrell estimates that from 20 to 50 per cent of the muds from the rivers are deposited beyond the 100-fathom line, and are thus permanently withdrawn from the lands. This estimate is entirely in harmony with the deficiency of clastics in geologic sections, and with the probable withdrawal of magnesium from the lands which is registered in the decreasing magnesium content of limestones in going up the geologic time scale. But the loss of muds from the lands may have been even greater in the past, since many large streams in various latitudes have submerged channels which in some cases extend to the edge of the 100-fathom line. On the other hand, the percentage loss of muds undoubtedly was relatively much less during periods of widespread continental submergence. But during such periods, the total mud transported was very much less, owing to the smaller relief of the lands and their floral blanket resulting from the moderate, equitable climatic conditions which appear to have accompanied the expansion of the seas. During such periods, muds were accumulating on the lands, until periods of continental uplift, like the present, accelerate their transportation toward the continental margins and the deep sea.

Does the ratio of calcium to magnesium in the sea show a selective loss of magnesium from the lands with geologic time?—The ratio of calcium to magnesium in the river waters of the world, taking

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[1] J. W. Barrell, *Jour. Geol.*, XIV, 346.

Clarke's data, is approximately 6:1. In the ocean, the ratio of calcium to magnesium is 0.35:1. The relative amount of calcium abstracted from sea water is evidently many times greater than that of magnesium. At the present time, a large proportion of the calcium is being deposited in the deep sea, and is thus either temporarily or permanently withdrawn from the land. A very large proportion of the calcium delivered to the sea has, however, been returned to the lands in the form of limestone deposits; in fact there seems to have been a relatively greater return of calcium carbonate to the lands than of the complementary clastics.

In view of the excess of limestone on the lands, it seems highly probable that the high magnesium content of the ocean represents a selective withdrawal of magnesium from the lands during geologic time. This may be one factor which could have caused a decline in the proportion of magnesium contributed to the sea, in the same way as the sodium contribution has declined with geologic time, because of its accumulation in the sea.

Résumé of results of sedimentation and their effect on the ratio of calcium to magnesium of the lands.—1. The marine sediments which are revealed to the geologist on the continental interiors were deposited during periods of widespread continental submergence. It is a significant fact that the sediments on the continental interiors probably represent several times as much limestone as could be gotten by redistributing an average igneous rock, or average rhyolite or basalt. The gain in limestone seems to be due mainly to a loss of the complementary shales and selective deposition of limestones on the continental interiors. The sedimentary mantle covers about three-fourths of the known area of the continents. The ratio of calcium to magnesium in the average igneous rock is about 1.37 to 1 (Clarke). The lowest ratio of calcium to magnesium in any group of limestones in Daly's[1] compilation is 2.93:1, and the maximum 56.32:1. The ratio of calcium to magnesium in Clarke's average limestone is about 5 to 1. The ratio of calcium to magnesium in the average shale (Clarke) is about 1.48 to 1; that of the average sandstone (Clarke), 5.5 to 1. The dominance of sedimentary over Archean and eruptive terranes and the high percentage of limestones over muds

[1] R. A. Daly, *Bull. Geol. Soc. of America*, XX, 153–70.

indicate a higher ratio of calcium to magnesium of the present lands than in the primitive lithosphere.

2. The marginal sediments show a tendency toward more intense anamorphism, a greater number of and more profound unconformities than those of the interior, and a dominance of clastics in those sediments which were deposited during continental expansion. More intense anamorphism[1] of the border sediments involves a selective retention of magnesium in them.

3. Marine sediments on the present continental shelves within the 100-fathom lineconsist predominantly of clastics, from 50 per cent to 70 per cent of the river-borne sediments being deposited here. This seems to afford a fair perspective of the nature of sedimentation during continental expansion.

4. Areally the calcareous deposits constitute a minority of the deep-sea deposits. The rate of accumulation of the terrigenous deep-sea muds is probably vastly greater than that of the calcareous deposits. Furthermore, a considerable portion of the calcareous deposits goes back into solution, and has therefore the potentiality of returning to the lands. The permanent withdrawal of terrigenous muds from the land areas unquestionably exceeds that of calcareous deposits. This selective withdrawal suggests one factor in the causation of the loss of muds from the continental interiors. Since muds not only tend to absorb more magnesium than calcium, but actually show a high magnesium content when compared to other sediments, it is not improbable that the permanent loss of muds from the continents also involves a selective and permanent loss of magnesium.

5. The selective retention of land-derived magnesium in sea water may have been an important factor in causing an increase in the ratio of calcium to magnesium of the lands.

HAS THE RATIO OF CALCIUM TO MAGNESIUM IN THE RIVER WATERS INCREASED WITH GEOLOGIC TIME?

The lands have been shown to represent a higher content of limestone than could have been gotten from the redistribution of the principal igneous rock types which are generally accepted as approximating the composition of the primitive lithosphere. In tracing the evolution of the limestones and dolomites to chemical changes in the sea, it is found highly probable that the ratio of calcium to magnesium in the streams is higher at the present time than in the streams of the primitive lands. This will develop from the following considerations.

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[1] *Ibid.*, 37, "Dynamic Metamorphism."

The influence of the terranes on the calcium magnesium ratio of underground water and streams.—Unfortunately the data on the calcium magnesium ratio of streams and underground water cannot be regarded as a satisfactory basis for correlation with the calcium magnesium ratio of the terranes over which they flow. The chances of error in water analysis and the variability of the composition of streams make a single analysis or even a group of analyses a questionable basis of correlation. The yearly average stream compositions based on daily samples gotten by the United States Geological Survey[1] for the streams of the United States east of the 100th meridian constitute a creditable exception.

Judging by the data available, it seems that underground waters and streams have a higher ratio of calcium to magnesium than the terranes through which they flow. This agrees with the fact that the metamorphism of rocks results generally in a higher percentage loss of calcium than of magnesium. From Orton's[2] figures, the average ratio of calcium to magnesium in the Niagara limestone of Ohio is 1.72. The rock waters as reported by Orton in the Niagara limestone have the following ratios of calcium to magnesium:

LOCALITY	Ca/Mg
Sidney, Ohio	4.0
Celina, Ohio	1.92
Fountain Park, Ohio	3.15
Fountain Park, Ohio	2.52
Plain City	2.55
Harrisburg	2.59

An average of 66 analyses of well waters from sandstones given in *Bull. 4*, of the University of Illinois, yields a ratio of calcium to magnesium of about 2.6. Twenty-four analyses of well water from dolomites gave an average calcium magnesium ratio of 2.3.

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[1] R. B. Dole, "Water Supply," *Paper 236, U.S.G.S.*

[2] Edw. Orton, *Nineteenth Ann. Rept. U.S.G.S.*, Part 10.

None of the crystalline terranes from which stream analyses are reported can be regarded as equivalent in composition to an average igneous rock, in which the ratio of calcium to magnesium is about 1.37 to 1.

The analyses are of unequal value. Only those of the Chippewa and Wisconsin are based on yearly averages. The calcium ratio of the others may be too high or too low. In the following table, the ratio of calcium to magnesium varies from 2.03 to 4.91.

TABLE XX

TABLE SHOWING THE CALCIUM MAGNESIUM RATIO IN STREAMS FLOWING OVER CRYSTALLINE ROCKS

River	Mg	Ca	Source
Arkansas River, Canyon, Colo	1	3.95	Clarke, *Bull. 330, U.S.G.S.*, 59
Pigeon R., Minn	1	3.14	*Ibid.*, 61
Ottawa R. Low water (*a*)	1	3.50	Daly, *Bull. Geol. Soc. Am.*, XX, 159
Ottawa R. High Water (*b*)	1	3.82	*Ibid.*
Ottawa R. mean (*a*) and (*b*)	1	3.69	*Ibid.*
Ottawa R. (St. Anne)	1	4.91	*Ibid.*
From granite terrane, average 6 analyses	1	3.20	J. Hanamann, "Bohemia," *Archiv. Natur-Landesforschung Böhmen*, IX, No. 4
From mica schist, av. 6 analyses	1	2.48	*Ibid.*, X, No. 5
Wisconsin River	1	2.03	Average of one year. Dole, *W.S. Paper, U.S.G.S.*, 236
Chippewa River	1	2.70	Average of one year. Dole, *W.S. Paper, U.S.G.S.*, 236

The following calcium magnesium ratios of streams on shales and dolomites are based on yearly averages of daily samples reported by Dole.

TABLE XXI

THE CALCIUM MAGNESIUM RATIO IN STREAMS FLOWING OVER DOLOMITE AND SHALES

River	Sample	Mg	Ca	
Fox River, Elgin, Ill	Niagara dolomite	1	1.70	Average of 1 year
Fox River, Ottawa, Ill	Niagara dolomite and Cincinnati shale	1	1.87	" " " "

TABLE XXI—*Continued*

River	Sample	Mg	Ca	
Kankakee, Kankakee, Ill.	Niagara dolomite	1	2.76	Average of 1 year
Rock, Rockford, Ill.	Dolomite and shale	1	1.80	" " " "
Rock, Sterling, Ill.	" " "	1	1.80	" " " "
White, Azalia, Ind.	" " "	1	2.65	" " " "
White, Indianapolis, Ind.	" " "	1	2.55	" " " "
Cedar, Cedar Rapids, Ia.	" " "	1	3.00	" " " "
Hudson, Hudson, N.Y.	" " "	1	5.50	" " " "
Wabash, Logansport, Ind.	" " "	1	2.34	" " " "
Wabash, Vincennes, Ind.	" " "	1	2.77	" " " "
Illinois, La Salle, Ill.	" " "	1	2.27	" " " "
Illinois, Peoria, Ill.	" " "	1	2.33	" " " "
Illinois, Kampsville, Ill.	" " "	1	2.35	" " " "
Iowa, Iowa City, Ia.	" " "	1	2.88	" " " "
Maumee, Toledo, O.	" " "	1	3.56	" " " "
Little Vermilion, Streator, Ill.	" " "	1	1.72	" " " "
Little Wabash, Carmi, Ill.	" " "	1	2.30	" " " "
Miami, Dayton, O.	" " "	1	2.45	" " " "
Cache, Mounds, Ill.	" " "	1	3.16	" " " "
Big Vermilion, Danville, Ill.	" " "	1	2.16	" " " "
Big Muddy, Murphysboro, Ill.	" " "	1	2.08	" " " "
Embarass, Charleston, Ill.	" " "	1	2.12	" " " "
Embarass, Lawrenceville, Ill.	" " "	1	2.30	" " " "
Grand, Grand Rapids, Mich.	" " "	1	2.94	" " " "
Muskingum, Zanesville, O.	" " "	1	4.52	" " " "
Sangamon, Decatur, Ill.	" " "	1	2.11	" " " "
Sangamon, Springfield, Ill.	" " "	1	2.16	" " " "
Sangamon, Chandlerville, Ill.	" " "	1	2.08	" " " "

The average calcium to magnesium ratio of these streams is between 2.5 and three. The ratio of calcium to magnesium of a normal dolomite is 1.61; that of an average shale 1.47 (Clarke). The calcium to magnesium ratio of the streams is probably higher than that of the terranes through which they flow.

An average of five water analyses on phyllite reported by Hanamann shows a ratio of calcium to magnesium equal to 2.37.

The stream waters from limestone areas show a high calcium ratio. See Table XXII.

TABLE XXII

TABLE SHOWING THE CALCIUM MAGNESIUM RATIO IN STREAMS FLOWING OVER LIMESTONE

River	Mg	Ca	Source
Thames	1	11.6	*Bull. 330, U.S.G.S.*, 75
Meuse, Liège, Belgium	1	10.8	*Ibid.*, 75
Seine at Bercy	1	46.0	*Ibid.*, 76
Loire at Orléans	1	10.7	*Ibid.*, 76
Rhone at Geneva	1	16.8	*Ibid.*, 76
Kentucky River, Frankfort	1	5.5	*Ibid.*, 66
Cumberland at Nashville	1	10.6	*Ibid.*, 66

The following table of averages suggests the influence of the terrane on the run-off.

TABLE XXIII

Terrane	No. of Analyses	Ca/Mg
Limestones	7	15
Phyllites	5	2.37 Hanamann
Crystalline	11	3.36
Dolomites and shales	29	2.91
Sandstone	66	2.6
Dolomite	24	2.3

The influence of climate on the calcium magnesium ratio of streams.—Clarke[1] has pointed out that the streams of humid, more or less forest-covered portions of North America are normally carbonate waters in which calcium is the principal base, while rivers in arid climates tend to be high in sulphates and chlorides in which calcium may or may not be the principal base. The magnesium content of streams in arid climates tends to be high, as shown by the following table.

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[1] F. W. Clarke, *Bull. 330, U.S.G.S.*, 72.

TABLE XXIV

CALCIUM MAGNESIUM RATIO IN STREAMS OF ARID COUNTRIES

Streams	Mg	Ca	Source
Sacramento R., Cal.	1	2.12	Clarke, *Bull. 330, U.S.G.S.*, 70
San Lorenzo R., Cal.	1	2.01	*Ibid.*, 70
Santa Clara R., Cal.	1	2.30	*Ibid.*, 70
Mission Creek, Cal.	1	3.83	*Ibid.*, 70
Cold Spring Creek, Cal.	1	3.01	*Ibid.*, 70
Mono Creek, Cal.	1	2.74	*Ibid.*, 70
Santa Ynez R., Gibraltar, Cal.	1	2.93	*Ibid.*, 70
Chelif R., Algeria	1	1.81	*Ibid.*, 70
Chelif R., Algeria	1	1.50	*Ibid.*, 70
Chelif R., Algeria	1	2.88	*Ibid.*, 70
Brazos R., Tex.	1	4.67	*Ibid.*, 69
Rio Grande, Tex.	1	7.20	*Ibid.*, 69
Pecos R., N.M.	1	3.72	*Ibid.*, 69
Colorado River, Yuma, Ariz.	1	3.30	*Ibid.*, 69
Gila River, Ariz.	1	3.17	*Ibid.*, 69
Salt River, Ariz.	1	2.65	*Ibid.*, 69
Colorado R., Austin, Tex.	1	3	Dole, *W.S. Paper 236, U.S.G.S.*, 56
Rio Grande, Laredo, Tex.	1	4.5	*Ibid.*, 96
Brazos, Waco, Tex.	1	6.3	*Ibid.*, 50

Where the terrane is exceptionally calcareous, however, calcium may predominate considerably. The insolubility of lime under arid conditions is illustrated by Hilgard's[1] composite soils, Table XXV.

TABLE XXV

CALCIUM MAGNESIUM RATIO IN SOILS FROM ARID AND HUMID REGIONS

Soil	Mg	Ca
Average of 466 soils from humid regions of southern part of United States	1	.57
Average of 313 soils from arid portions of United States	1	1.15

Apparently soils in arid climates contain about twice as much calcium in proportion to magnesium as those of humid climates.

Influence of the belt of cementation on the calcium magnesium ratio of underground waters.—The materials carried in solution by underground waters in the belt of cementation undergo various abstractions and additions on their way to the sea. The cements of the limestones and sandstones undoubtedly contain much more calcium than magnesium, although no estimate of their relative proportions can be given. Since the ratio of calcium to magnesium in the average sandstone (Clarke's) is 5.50 to 1, it is probable that the ratio of calcium to magnesium of the cementing materials in the sandstones is even higher.

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[1] E. W. Hilgard, *Bull. No. 3, U.S. Weather Bureau* (1892), 30.

The solutions which percolate through shales, clays, and other silicates are known to suffer an exchange of bases and other changes through the interaction of water solutions and silicates. This interaction is dependent upon the condition of chemical equilibrium between the solutions and the silicates. Kiilenberg[1] and other experimenters have shown that soils absorb more potassa and magnesia than lime and soda. The great absorption of potassa by soils and the very slight absorption of soda has been interpreted as the reason why land plants utilize potassa more largely than soda.

TABLE XXVI

RATIO OF CALCIUM TO MAGNESIUM IN THE CHLORIDE WATERS OF THE DEEP COPPER MINES OF MICHIGAN, AS COMPARED WITH THE SURFACE WATER

Deep Mine Waters	Ratio of Ca: Mg
C. and H. vertical shaft	62
Tamarack Junior (very strong)	319
C. and H., 3,000 feet	412
C. and H., 17th level	475
Tamarack, 4.300 feet	(trace of magnesium present)
Trimountain, 9th level	(trace of magnesium present)
Quincy mine (very strong)	4,300
Quincy mine	3,078
Surface water	4.75

The influence of silicates in the belt of cementation on the calcium magnesium ratio of underground waters is suggested by a comparison of the calcium magnesium ratio of the surface and deep waters of the copper mines of Lake Superior. The deep waters are probably the modified residuum left from the cycle of deposition which developed the ores and gangue minerals. The result of cementing processes has been a concentration of calcium in the solutions. Magnesium has evidently been forced out of solution by the conditions of chemical equilibrium. See Table XXVI.

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[1] *Mitteil. d. Landw. Centralvereins für Schlesien*, Heft 15, p. 83, quoted by E. C. Sullivan, *Bull. 312, U.S.G.S.*, 16–19.

The relative absorptive power of the crustal materials for calcium and magnesium has not been adequately determined. Certain it is that many shales, slates, muds, and soils have a higher content of magnesium than of calcium. The probability that the selective withdrawal of muds from the lands to the deep sea has involved a selective loss of magnesium from the lands has been pointed out on p. 414.

The average calcium magnesium ratio of the solutions contributed to the sea.—The Mississippi[1] at New Orleans, which may be regarded as a mixture of the waters from the average Paleozoic terrane, shows a ratio of calcium to magnesium of 3.81 to 1. The average calcium to magnesium ratio of 73 streams east of 100th meridian of the United States observed daily at 94 stations for a period of one year is about 4 to 1. In Sir John Murray's well-known composition of 19 streams of the world, the calcium to magnesium ratio is 4.4 to 1. From Mellard Reade's[2] data, the ratio of calcium to magnesium in the materials of chemical denudation is 8.25 to 1. A better based figure for the average composition of the streams of the earth is that recently made by Clarke.[3] The ratio of calcium to magnesium in Clarke's average as previously cited is about 6 to 1.

While the ratio of calcium to magnesium of the solutions contributed to the sea is higher than it would be if the lands had the composition of an average igneous rock, the largest streams do not seem to show the high calcium to magnesium ratio that one would expect from the amount of limestone on the continents. However, the Mississippi is about the only large stream whose composition is accurately determined. It may be that the large amount of suspended material in rivers tends to lower the calcium ratio, since the muds, particularly of humid climates, tend to be high in magnesium. The arid nature of about one-fifth of the land area is another factor which may cause a retention of calcium by the land. If this hypothesis is correct, a compensating increase in the calcium ratio of rivers will be contemporaneous with oceanic expansion.

[1] R. B. Dole, *W.S. Paper 236, U.S.G.S.*, 117.

[2] Mellard Reade, *Chemical Denudation in Relation to Geologic Time* (1879), 1–61.

[3] F. W. Clarke, *Study of Chemical Denudation*, Smithsonian Institution, Vol. LVI (1910), No. 5, p. 8.

Conclusion: Increase of the ratio of calcium to magnesium in rivers with geologic time.—Evidence has been presented to show that the ratio of calcium to magnesium of stream water is influenced primarily by the ratio of calcium to magnesium of the terranes which they drain, being generally higher than that of the terranes. Climate exerts a modifying influence. Aridity lowers the ratio of calcium to magnesium of the stream waters, causing a concentration of calcium in the soils, while humidity has the opposite effect. The interaction of the salts carried in solution by streams and ground waters with the land materials, particularly those high in clay, results in a greater loss of magnesium from the waters than of calcium, thus tending to increase the ratio of calcium to magnesium of the streams and ground waters.

Regardless of any theory of the origin of the earth, geologic evidence points to the igneous rocks as the primitive source of the sedimentary rocks. The streams of the primitive lithosphere, therefore, probably approached in their chemical character the present streams, flowing over crystalline rocks, subject to climatic and other modifications. Such streams have a ratio of calcium to magnesium approximating 3 to 1. The best figure given for the average calcium to magnesium ratio of the streams of the world is approximately 6 to 1. The latter figure probably should be greater, considering the abundance of limestone on the continents. Little doubt therefore remains that the proportion of calcium to magnesium in the streams is now higher than in earlier stages of the earth's history. It is also highly probable that the increase in the ratio of calcium to magnesium in the rivers has been continuous with geologic time, because of the progressive increase in this ratio in the limestones deposited during geologic time, and because of the selective deposition of limestones on the submerged continents.

STATEMENT OF HYPOTHESIS

The conclusion has been reached that dolomites develop predominantly in the sea rather than by the metamorphism of limestones after their emergence from the sea. Hence the decline in the percentage of dolomite in going up the geologic column seems to indicate that less and less dolomite was deposited in successive periods of geologic history, thus pointing to a progressive change in the conditions of deposition. Of the four factors controlling the deposition of carbonates in the sea, viz., temperature, pressure, life processes, and chemical composition, only the last two show any probability of progressive change with time. There is no evidence for a change in the nature of life processes. There is evidence for a change in the chemical composition of the sea, specifically for an increase in the ratio of calcium to magnesium contributed to the sea from the lands, which will appear from the following considerations. The present lands contain a much larger proportion of limestones than could be gotten by redistributing a granite or basalt, generally accepted as being equivalent to the materials of the primitive lands. It is inferred from a consideration of the relation between the composition of river waters and the terranes which they drain that the present rivers have a higher ratio of calcium to magnesium than those of the primitive lands.

The accumulation of limestones on the lands of increasing calcium content, with time, seems to be related to a reworking of the land over and over again along certain selective lines. A higher percentage of calcium than of magnesium tends to be lost from all kinds of rocks when subjected to all kinds of metamorphic processes. Hence there is a continuous selective removal of calcium from the lands of the sea, as is evidenced by the fact that the ratio of calcium to magnesium of rivers tends to be higher than the ratio of calcium to magnesium of the lands which they drain. This involves a selective retention of magnesium in the clastics. The transportation and deposition of clastics is at a maximum during periods of continental expansion and at a minimum during periods of continental submergence. The clastics are therefore deposited mainly on the margins of the continents and in the deep sea. Those deposited in the deep sea are permanently lost to the lands and with them goes a selective loss of magnesium from the lands. The carbonates, calcium and magnesium, are deposited mainly in shallow epicontinental seas during periods of continental submergence, in consequence of organic and inorganic agencies. The percentage of calcium carbonate which is deposited from the sea is higher than that of magnesium carbonate, and from field and laboratory evidence it is inferred that the proportions of the two carbonates deposited are in some direct relation to their proportions in the rivers which bring them to the sea. Hence, there is a selective return of calcium to the lands.

It is therefore inferred that the evolution of the limestones and dolomites has been in response to the gradual increment of calcium over magnesium in the solutions contributed to the sea, a tendency arising primarily from physical-chemical causes, aided or accelerated by organic processes working harmoniously with the inorganic environment.

For illustration, it may be assumed that sedimentation began during continental expansion when the lands had the composition of an average igneous rock. From the known results of metamorphic processes, it would follow that the solutions contributed to the sea had a higher calcium to magnesium ratio than the lands from which they were derived, and that the residuals had a higher proportion of magnesium to calcium than the original rocks. A part of the residuals, particularly the muds, are subject to selective transportation to the continental margin and the deep sea. Accepting the hypothesis of the permanence of oceans and the continents, those deposited in the deep sea are permanently removed from the continents. The calcium and magnesium salts interact with the materials of the ocean bottom and enter into the constitution of silicates, carbonates, and other compounds, or they may interact with other constituents in the water, and be precipitated principally as the carbonates. Magnesium would tend to interact more actively with the muds of the bottom than calcium. Calcium would tend to be more insoluble in shallow water than in the deeps, while the opposite tendency probably characterizes magnesium. Magnesium salts in general are more soluble in sea water than calcium salts. Organic precipitation, apparently only an adaptation to conditions of chemical equilibrium already existing, would be particularly effective in abstracting calcium from warm, shallow seas. The relative solubility of the materials precipitated would depend upon conditions of equilibrium controlled mainly by temperature, concentration, the amount of carbonic acid in the air and ocean, and organic processes. As a result of the preceding selective influences, the calcium to magnesium ratio of the limestones would tend to be higher than that of the solutions contributed to the sea. However, contemporaneous with continental expansion, as at the present time, limestone deposition would be at a minimum, which might involve a concentration of calcium in the sea until more favorable conditions of precipitation arise. Limited areas of shallow water, vigorous erosion, continental climates, and other supplementary conditions make periods of continental expansion more favorable to the deposition of clastics than limestones.

Gradually the lands waste away, the ocean advances over the continents, partly in consequence of fill from the land, in part, perhaps, as a result of secular earth movements which cause a shallowing of the ocean basins. The rivers carry less and less débris to the sea, and deposit it farther and farther inland from the margin. On the submerged continental areas, covered by shallow seas, which now may be three or more times as extensive as they were during the preceding period of continental expansion, chemical and biochemical processes combine in making this an era of limestone building. From experimental and field evidence, the inference is drawn that *the ratio of calcium to magnesium in the deposited limestones is influenced primarily by their respective rate of contribution from the land, and modified by selective organic and inorganic agencies working to a common end.*

As postulated by Chamberlin, with the expansion of the seas, the zonal, diversified continental climates tending toward aridity and refrigeration yield to more uniform, mild atmospheric conditions. A widening of the life zones favorable to limestone deposition follows. Thus in the Devonian, corals thrived in the now ungenial climate of Hudson Bay. With world-wide climatic moderation, a new condition of equilibrium is established between the carbon dioxide of the sea and air. Warm water absorbs less carbon dioxide than cold. The sea begins to contribute its excess of carbon dioxide to the air, in consequence of which the calcium of the sea becomes still more insoluble. The atmospheric conditions and the land relief favor the floral blanketing of the earth, thus stimulating chemical denudation and creating an effective screen for the retention of clastic materials on the land.

As the waters again withdraw from the lands into the hollows of the sea in response to secular earth movements, they leave composite sediments behind them whose ratio of calcium to magnesium is higher than that of the average igneous rock. With topographic rejuvenation, the muds are again carried toward the margin and to the deep sea, or possibly at times directly to the deep sea as suggested by submerged stream channels, the continuation of existing streams which in some cases extend to the margin of the deep sea. Various parts of the earth are subjected to regional metamorphism and secular uplift, particularly the continental margins, causing selective removal of calcium and the concentration of magnesium in the residuals. The marginal sediments, dominantly clastics, by virtue of position, relief, and a combination of other factors, are in a most favorable position to be removed from the land and swept into the deep sea, where they would be permanently withdrawn from the land. The deposition of clastics is again at a maximum, that of limestones at a minimum. As the pendulum swings from one extreme to another, it marks a curve of progressive change in the composition of the lands and in the ratio of calcium to magnesium in the salts contributed to the sea, consummated by an accumulation of limestones on the continents of progressively higher calcium content, both a reflex and a cause of changes in the land composition, and by the withdrawal of the complementary muds toward the margins and the deep sea, slow during periods of oceanic expansion, but tremendously accelerated during periods of oceanic retreat, selective concentration of magnesium in the deep zones of high temperature and pressure, in the clastics, and in the sea—a never-ending cycle of selective causes and cumulative effects, recalling the words of Faust:

> Wie alles sich zum Ganzen webt,
> Eins in dem anderen wirkt und lebt.

SUMMARY

The problem under discussion is, Why does the dolomite content of the geologic column decrease with time? Is it due to a secondary alteration of limestone after emergence from the sea, roughly proportional to time, or is it due to a gradual decline in the primary development of dolomite in the sea? If the latter, what factors controlling the deposition of dolomite have changed during geologic time, temperature, pressure, life processes, or the chemical composition of the sea?

The conclusions reached are: dolomite develops predominantly in the sea, therefore the decrease in the dolomite content of the sediments in going up the geologic column is mainly due to a decrease in the proportion of dolomite developed in the sea with time.

The factors of deposition whose progressive change has probably controlled the decline of dolomite development in the sea are life processes and the chemical composition of the sea. There is no definite evidence for a change in the nature of the life processes in their relation to dolomite deposition. There is evidence for a change in the chemical composition of the sea; namely, the fact that the present ratio of calcium to magnesium of the streams is probably more than twice that of streams draining crystalline terranes, comparable in composition to the primitive lands. Accepting uniformitarianism, it follows that the present streams have a much higher ratio of calcium to magnesium than the primitive streams. It has been indicated that solutions high in magnesium and low in calcium are more favorable to the development of dolomite than those which are low in magnesium and high in calcium. It is therefore highly probable that the chemistry of the primitive sea was more favorable to the deposition of dolomite than the present ocean.

The increase in the proportion of calcium to magnesium in the streams is believed to be due to selective processes whose effects have been cumulative with time. Rock alterations tend to result in a higher percentage loss of calcium than of magnesium, the materials lost being largely transported in solution to the sea.

A higher percentage of magnesium is retained in the residuals of rock decay than calcium, but erosive processes are constantly removing the residuals toward the margins of the lands, and during periods of continental expansion a considerable proportion is swept into the deep sea and permanently lost from the lands. In consequence of a combination of organic and inorganic agencies, the maximum deposition of limestones and dolomites is on the submerged lands during periods of oceanic expansion. The percentage of calcium precipitated is higher than that of magnesium, but the proportions of calcium to magnesium which are precipitated bear some direct relation to their ratio in the rivers which bring them to the sea. With the progressive elimination of clastics and magnesium from the lands with geologic time, and in their place the gradual accumulation of calcium in the form of limestone, the proportion of calcium to magnesium contributed by rivers to sea has increased with time.

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